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Production of renewable phenolic resins by thermochemical conversion of biomass: A review

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Abstract

This review covers the production and utilisation of liquids from the thermal processing of biomass and related materials to substitute for synthetic phenol and formaldehyde in phenol formaldehyde resins. These resins are primarily employed in the manufacture of wood panels such as plywood, MDF, particle-board and OSB. The most important thermal conversion methods for this purpose are fast pyrolysis and vacuum pyrolysis, pressure liquefaction and phenolysis. Many feedstocks have been tested for their suitability as sources of phenolics including hard and softwoods, bark and residual lignins. Resins have been prepared utilising either the whole liquid product, or a phenolics enriched fraction obtained after fractional condensation or further processing, such as solvent extraction. None of the phenolics production and fractionation techniques covered in this review are believed to allow substitution of 100% of the phenol content of the resin without impacting its effectiveness compared to commercial formulations based on petroleum derived phenol. This survey shows that considerable progress has been made towards reaching the goal of a price competitive renewable resin, but that further research is required to meet the twin challenges of low renewable resin cost and satisfactory quality requirements. Particular areas of concern are wood panel press times, variability of renewable resin properties, odour, lack of reactive sites compared to phenol and potential for increased emissions of volatile organic compounds.
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Keywords: Pyrolysis liquids; Thermolysis liquids; Resins

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Contents

1. Introduction and scope of review

Increasing petroleum prices, concerns over security of supply and concerns about climate change are major drivers in the search for alternative renewable energy sources. Biomass is a primary candidate because it is the only renewable source of fixed carbon, which is essential in the production of conventional hydrocarbon liquid transportation fuels and many consumer goods.

Lignocellulosic biomass is made up of three main components: hemicellulose, cellulose and lignin, of which the lignin fraction can account for up to 40% of its dry weight [1,2]. Lignin is of particular interest due to its phenolic nature from which a wide variety of phenols and phenol derivatives and aromatic chemicals can be derived. Notable among the interest in use of lignin derived material is utilisation as a substitute for phenol in phenol–formaldehyde based wood panels. There has been particular interest in the use of pyrolytic lignin as a renewable resin from pyrolysis of biomass due to the high yield of pyrolytic lignin and its ease of assimilation into phenol formaldehyde formulations. This interest is enhanced by the fact that high lignin content biomass is widely available, often at low cost and in large quantities, while phenol is a relatively expensive bulk chemical that is manufactured from increasingly costly crude oil.

Previous reviews have been published on fast pyrolysis processes [2,3], applications of fast pyrolysis liquids including resins [4] and on the production of monomeric phenols by thermochemical conversion of biomass [5]. Amen-Chen et al. [5] focussed on the thermal behaviour of isolated lignins and lignin model compounds in order to better understand the complex chemistry leading to the formation of single-ring phenolic compounds. They suggested that analytical thermolysis of the model lignins provides useful information for optimising production variables to achieve greater yields of particular phenolics, notably guaiacol, syringol and their derivatives. The production of monomeric phenols through hydrogenation of lignin has been the subject of much research, some of it indicating the

potential for substantial yields of phenol and benzene [6], but this area of research has been excluded from the present review. Mohan et al. [7] have also recently reviewed pyrolysis of biomass for bio-oil, including fractionation techniques for the recovery of a variety of chemicals. Another route to aromatic chemicals from biomass is the use of catalysts and zeolites in particular. This route does not require the biomass to contain lignin, as the aromatics can be synthesised from vegetable oil or starchy feedstocks [8] and is also excluded from the scope of the present review.

This review focuses on production of phenolics by fast and vacuum pyrolysis, liquefaction and phenolysis, and also covers fractionation methods for the recovery of concentrated fractions of phenolics. The manufacture and use of resins for the production of actual boards are described to explain the quality impact of partial or complete substitution of petroleum-derived phenol. The thermal conversion methods considered in this review require the biomass to contain lignin to achieve a phenolics-rich product. Consequently, only lignocellulosic biomass feedstocks, lignin-enriched biomass fractions and lignin are considered.

2. Biomass feedstocks for production of phenolics

Woody biomass primarily consists of hemicellulose, cellulose and lignin. It also contains small amounts of organic extractives and mineral matter. The amount of lignin in wood varies depending on a number of factors, including tree species, climate and soil conditions. Typically it makes up between 19% and 35% of the dry wood weight [7]. When heated, the lignin component depolymerises to form monomeric and oligomeric phenolic compounds. The most widely employed feedstocks to date for production of pyrolytic lignins are hard and softwoods due to consistency, widespread availability and extensive referencing. In addition lignin and lignin enhanced biomass are difficult to characterise and to thermochemically process. Apart from woody biomass many other biomass feedstocks have been used in the production of phenolic precursors for the manufacture of phenol-based resins. An overview is provided in Table 1. The feedstocks in the table are arranged into five categories: woods, forest, industrial and agricultural residues, and industrial lignins.

Table 1
Feedstocks tested for the production of reactive phenolic compounds using any of the thermal conversion methods covered by this review

Feedstock	Type of feedstock	Refs.
Woods	Softwood bark, ground softwood, pine, sawdust woodchips	[5,23–26,30–31,37–43,56,59]
	Hardwood, mixed hardwoods	[5,23–31,37,56]
Forest residues	Bark waste, peat moss, treetops, limbs	[42,58]
Agricultural residues	Bagasse, cashew nut shell, corn bran	[35,49,53]
Industrial residues	Lignin from newsprint, paper waste, creosote treated wood waste, birch wood waste, wood industry residues, black pulping liquor	[35,43–50]
Industrial lignins	Organosolv lignin, lignin from steam explosion of birch, lignosulphonate	[51,52,54,55]

Softwoods may yield more reactive phenolics than hardwoods due to the relative lack of syringols with one methoxy group in softwood derived liquids compared to guaiacol with two methoxy groups derived from hardwood [9] as shown in Fig. 1 and explained below. Moreover the lignin content of softwoods is generally higher than the lignin content of hardwoods [10,11,14] as shown in Table 2. Softwood lignins are predominantly (usually more than 95%) derived from coniferyl alcohol whereas the lignins of hardwood are based on a mix of coniferyl and sinapyl alcohol. The chemical formulae of syringol, guaiacol and their precursor alcohols are shown in Fig. 1 to illustrate that guaiacol has one extra site available for polymerisation. The major chemical functional groups in lignin include hydroxyl, methoxyl, carbonyl and carboxyl in various amounts and proportions, depending on genetic origin and extraction processes. For bark [12] and coconut husk [13] it has been reported that high pressure and temperature alone are sufficient to make boards, as the phenolic compounds naturally present in these feedstocks bind the particles.

Table 2 shows the proximate composition of woods and barks [14]. Industrial lignins (Table 1) and lignosulphonates in particular, have also been used directly for resin syntheses without prior treatment. The reactivity of these lignins is generally very low and they tend to be used as extenders or fillers, typically making up less than 10% of the resin, as press times otherwise become excessively long. The direct use of lignins for resin

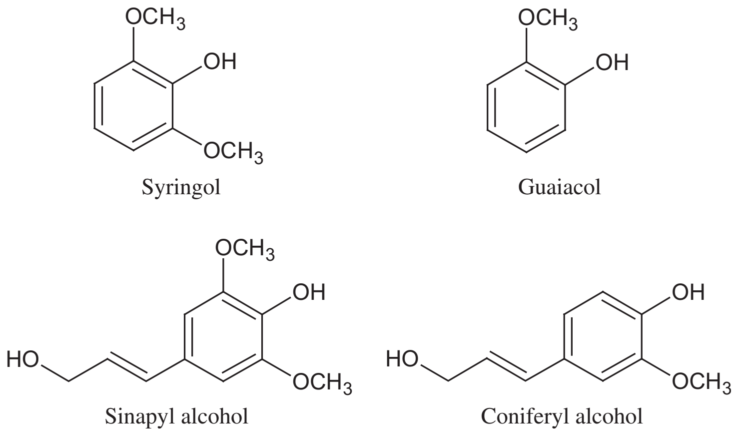


Fig. 1. Chemical formulae for syringol, guaiacol and their precursor alcohols.

Table 2
Typical proximate composition of wood and bark [14]

Compounds (wt%)	Softwood		Hardwood	
	Wood	Bark	Wood	Bark
Lignin	25–30	40–55	18–25	40–50
Polysaccharides (hemicellulose and cellulose)	66–72	30–48	74–80	32–45
Extractives	2–9	2–25	2–5	5–10
Ash	0.2–0.6	Up to 20	0.2–0.6	Up to 20

synthesis falls outside the scope of this review. This area is well covered by the following reviews: Doering et al. [15]; Chen [16]; Ringena [17]. This review does not cover direct use of industrial lignins for resin synthesis. Thermal conversion methods have only been applied in a few cases and in those the source and type of lignin are given in this review.

3. Phenolic compounds in bio-oils

Pyrolysis oils are a complex mixture of water, higher molecular weight lignin fragments and lower molecular weight organics. Considerable work has been done on analysing bio-oil from fast and vacuum pyrolysis [4–7,10,11,18–20]. Bio-oils contain up to 45% oxygen, and oxygen is a component of most of the more than 300 compounds that have been identified in pyrolysis oils [7]. Water is the most abundant compound, typically followed by hydroxyacetaldehyde (up to around 10 wt%), and acetic and formic acid (up to around 8 wt%). Bio-oil compounds have been classified into the main categories of hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolics. The concentration of phenol itself is typically very low, of the order of 0.1%, while GC analysable monomeric phenols typically range around 1–4 wt% [19]. The majority of the phenolics are too high in molecular weight to make the cut for GC analysis and are present as oligomers containing varying numbers of acidic, phenolic and carboxylic acid hydroxyl groups as well as aldehyde, alcohol and ether functions. The molecular weight of the oligomers ranges from several hundred to 5000 g/mol depending in particular on pyrolysis process severity (temperature, residence time, and heating rate profiles). Bio-oil compounds can be separated according to their water solubility. The addition of water yields an aqueous and an organics dominated phase, the former containing water and water-soluble materials (high-polarity compounds) and the latter containing water-insoluble materials (low-polarity components). The majority of the water-insoluble materials are lignin-derivative compounds. When the phase separating procedure involves the addition of drops of bio-oil to a large amount of water, followed by filtration and drying of the filtrate, the resulting insoluble fraction is commonly referred to as pyrolytic lignin and has been shown to be near exclusively lignin derived [4,10,11,20]. Typical pyrolytic lignin yields on a wet bio-oil basis are between around 10 wt% and around 30 wt% for a wood derived bio-oil [10].

Amen-Chen et al. [5] reviewed the production of monomeric phenols from thermolysis of biomass. They concluded that the yields of phenolic compounds such as guaiacol, syringol and their alkyl-derivatives depend on the use of appropriate conditions such as small wood particle size, low reactor residence time, reduced pressure and moderate pyrolysis temperature. For example, to illustrate the effect of temperature in a study of analytical pine pyrolysis, phenolic aldehydes and alkylguaiacols were the main products of pyrolysis at 400 °C while at 600 °C phenolic aldehydes were converted to catechol and alkylphenols [21]. High temperatures (800–1000 °C) resulted in an increase of aromatic hydrocarbons while phenolic aldehyde and alkylguaiacol yields were considerably reduced. Similarly, in another study pyrolysis temperature affected total monomeric phenols and liquid yields [22]. The optimum yield of monomeric phenols was 12 wt% (dry wood basis) at a pyrolysis temperature of 545 °C. Chemical analysis of the pyrolysis oils indicated a high abundance of phenols, cresols, ethyl phenols, xylenols and trimethylphenols.

4. Phenolic resins from fast pyrolysis liquids

Fast pyrolysis is a relatively recent thermochemical conversion technology. Its defining characteristics are: moderate reaction temperatures, usually between 400 and 600 °C, rapid heating rates and short vapour residence times before condensation of the liquid products, typically below 5 s. This combination of features gives very high liquid yields, up to roughly 75 wt% on a dry basis for clean, low ash content woody biomass. Attempts to use this liquid for the production of renewable phenolic resins are described in this section.

Chum et al. [23–26] investigated pyrolysis oils derived from softwood, hardwood, and bark residue. They synthesised resins of both the novolac and resole varieties. Novolacs are a type of phenol–formaldehyde resin prepared by using an acid catalyst instead of a basic catalyst and the phenol to formaldehyde ratio used is below 1 which is lower than the ratio needed for a resole-type resin, which is always above one. Fast pyrolysis trials were carried out in a small vortex reactor with a capacity of 10–20 kg/h operated at 480–520 °C to produce optimum yields of pyrolysis oil (55 wt% on a dry basis). The vortex reactor transmitted very high heat fluxes to the biomass causing primary depolymerisation of the constituent polymers into monomers and oligomers. Pyrolysis oil was obtained after condensation of the vapours in a series of condensers. The first condenser was at 20 °C, the second condenser at 2 °C and the third and final condenser at −17 °C. Details of the pyrolysis process have been documented [27]. The remaining gas and aerosol stream was passed through a coalescing filter to remove the aerosols. Reactive components for resin synthesis were obtained by fractionating the pyrolysis oils and isolating phenolic and neutral fractions. Further detail is provided in Section 8.1 of this review, which covers bio-oil fractionation procedures. The phenolic and neutral components were used directly for phenolic-based adhesives i.e. Novolac and resole resins. The resins were evaluated and tested for wood panel production. The fraction containing phenolic and neutral components was not only to substitute phenol but also some of the formaldehyde used during resin synthesis making use of the aldehyde groups in the neutral fraction.

Direct use of fast pyrolysis oils without any product separation required to remove non-reactive fractions for PF resin was evaluated by Himmelblau from Biocarbon Co. [28,29]. Fast pyrolysis of mixed hardwoods (maple, birch, beech) was performed in an air-blown bubbling fluidised-bed to produce pyrolysis oils claimed to be suitable to directly make PF resins. While strictly speaking this is not a pure pyrolysis process, as a small amount of air is employed, the oxygen only represents an order of 5% of stoichiometric combustion requirements and the process is therefore quite close to standard fast pyrolysis.

The pyrolysis was carried out at 590 °C well above the oil maximising temperatures typically used by fast pyrolysis processes accepting lower oil yields but, it was claimed by Himmelblau, with 100% selectivity. Himmelblau did not explain what he meant by 100% selectivity. Char and ash contents in the oil measured were <1 wt%. Analysis of the pyrolysis oil identified about 40 compounds present at greater than 1% mol representing 82% mol of the material. Identified compounds are claimed to be all polymerisable with, on average, two positions available for methylene linkages versus three for phenol. As a consequence resins with a phenol substitution of 50% could still provide sufficient linkages for water resistant adhesives. These resins were said to perform nearly as well in making 3-ply plywood of southern pine as a commercial alternative. There is no independent confirmation of these results. It is striking, however, that no cellulose derived compounds are reported in the oil, and that a mixture of hardwoods is claimed to yield phenolics with

an average of two reactive sites, when ordinarily a large fraction of syringols would be expected.

Giroux et al. [30,31] from Ensyn investigated a method of preparing phenolic precursors by liquefying wood, bark and forest and wood industry residues using a patented fast pyrolysis process. Ensyn's technology has been dubbed Rapid Thermal Processing or the RTP^{TM} process. The method and apparatus for the fast pyrolysis of carbonaceous materials using this process are described in detail in the patent and other publications [32,33]. In the Ensyn RTP^{TM} process, wood or other biomass material is fed into a heated vessel where it is contacted with a stream of hot sand involving rapid mixing, high heat transfer rates and precisely controlled short uniform residence times. There is essentially no combustion occurring in this vessel since air input is minimised. At a temperature of around 500 °C the turbulent hot sand instantly flashes the biomass. A cyclonic hot solid recirculation system separates the solids from the non-condensable gases and primary product vapours and returns them to the mixer. The vapour is then cooled, condensed and recovered as a liquid product. For the commercial process a typical mass balance is 75% liquid bio-oil, 13% char and 12% combustible gas. These yields are by mass-weight and are as a percentage of dried wood (typically to a moisture content of about 8%).

Reactive bio-oil compounds were recovered and processed by distillation, evaporation or a combination thereof in order to obtain natural resin precursors, either as liquids or as solids. Distillation and/or evaporation processes were carried out in particular to remove acidic and odour bearing compounds [30,31]. The reactive fraction so obtained is referred to as 'natural resin' and comprises a total phenolic content from roughly 30–80 wt% and is according to Ensyn a highly reactive lignin compound that has been found to be suitable for use within resin formulations without requiring any further fractionation procedure. Designed resole resins comprising up to 60% of the natural resin precursor were prepared and tested in board production and found to exhibit similar properties as those of a commercially available resin used as a control. The natural precursor can be a substitute for phenol, or for both phenol and formaldehyde within phenol-containing resins. Similarly it is claimed that the natural resin precursor can replace a substantial part of the components within urea-containing resins.

Nakos et al. [34] from ACM Wood Chemical plc used pyrolysis oil as a substitute for petroleum derived phenol in resole resins. The feedstock for the pyrolysis oils was either bark or wood. No further information on the pyrolysis process was provided. Phenolic resins were developed using whole pyrolysis oil. Phenol substitution levels of up to 50% were achieved. Compared to the synthesis of the standard resin reaction conditions had to be modified when adding bio-oil. The resole-type resin was successfully used in the production of OSB and plywood. Compared to a commercial control, it had comparable or even superior wood adhesive properties. Higher phenol substitution was considered to likely be possible with a fraction enriched in reactive phenolics.

Apart from the use of pyrolysis oils on their own as a source of phenolics, Vergopoulou-Markessini and Tsiantzi [35] investigated phenol-based resins relying on naturally derived phenolics from a number of sources, for example a mixture of pyrolysis oil and/or cashew nut shell liquids (CNSL), and/or lignins. No information on the pyrolysis process, not even the feedstock, was provided. Cashew nut shell liquid is a dark natural liquid comprised of unsaturated alkenyl substituted phenols. The dual phenolic and alkenyl nature of CNSL makes it an ideal natural raw material for the synthesis of water-resistant resins and polymers [36]. As a lignin source, alkaline spent liquor from the pulping industry was used.

The combination of at least two natural sources of phenolics resulted in a synergistic effect and enabled phenol substitution levels of up to 80%. They also suggested that combinations involving tannin resins and diphenylmethane diisocyanate might be advantageous. These invented natural resins are claimed to be suitable for a range of manufacturing composite products such as particle boards, fibreboards (medium- and high-density fibreboards, MDF and HDF, respectively), OSB and plywood. While these patented results appear to show great promise, it should be stressed that again there is no independent confirmation of these results and no commercial use appears to have resulted from the patent to date.

5. Phenolic resins from vacuum pyrolysis liquids

In addition to fast pyrolysis, vacuum pyrolysis has been investigated as a means of producing phenolic resin precursors from lingo-cellulosic materials. Compared to fast pyrolysis, longer residence times, of the order of 40 s, are employed in vacuum pyrolysis. The vacuum suppresses condensation reactions in the vapour, as the concentrations of reactants and therefore reaction rates are lower. This effect is, however, not capable of fully compensating for the longer residence times, as evidenced by the fact that typically lower liquid yields are reported for vacuum pyrolysis compared to fast pyrolysis.

Roy et al. [37] investigated the production of a phenolics-rich pyrolysis oil for direct use in making resole resins. Pyrolysis oils were derived from softwood bark waste pyrolysed at $<550\,^{\circ}C$ under <50 kPa to produce vapours. The vapours were then condensed to obtain a condensate consisting of a phenolics-rich pyrolysis oil having a dew point of around 65–75 °C under 15–20 kPa. Under these condensation conditions, pyrolysis oils had fewer polymerised components, fewer acids and relatively reduced smoky odour levels. Vapours not condensed in this first step were condensed in a second step and additional processes such as evaporation were applied to recover a further phenolics fraction with a boiling point above 125 °C. A resole resin prepared from the phenolics-rich pyrolysis oil with 40% phenol substitution was used for the manufacture and evaluation of OSB panels. Mechanical properties (i.e. IB, torsion shear) were superior to those of the control panels prepared with a commercial resin [38].

Amen-Chen et al. [39] evaluated vacuum pyrolysis oils as phenol substitutes for resole-type resins. The pyrolysis oils were incorporated directly with formaldehyde during resin synthesis and no separation or fractionation processes were required except for the removal of low molecular weight organic acids. Pyrolysis oil was produced in a pilot plant scale vacuum reactor at 505 °C and 18 kPa with a feed rate of 50 kg/h. As a feedstock, softwood bark from balsam fir, white spruce and black spruce, was used and yielded 28 wt% of oil, 27 wt% of char, 17 wt% of gas and 25 wt% of pyrolytic water. In addition to the pilot plant pyrolysis unit, bark derived oils were also produced in an industrial demonstration reactor operating at 450 °C and a total pressure of 22.5 kPa, with a feed rate of 1000 kg/h. The technology is known as the Pyrocycling process and was commercialised by Pyrovac Inc. as described elsewhere [37]. Resole resins were prepared at petroleum phenol replacements of 25 and 50 wt% using the bark derived oils with formaldehyde to phenol ratios of 2.25, 2.0 and 1.75. Strandboards manufactured with the resins exhibited mechanical properties such as modulus of rupture, modulus of elasticity and internal bonding better than those specified in the Canadian Standards. The thickness swelling test of the boards did not meet the standards. No significant difference in panel performance

was observed between pyrolysis oils produced in the pilot plant and in the industrial scale pyrolysis unit. The resins having 25 wt% phenol replaced by pyrolysis oils were found to be suitable as surface resins and the performance was comparable to that of the commercial resin. Substitutions of up to 50 wt% of phenol with the pyrolysis oil reduced the cross-linking of the resin which was evident in lower internal bonding properties. The resins showed slower curing kinetics and lower thermal stability than those of the commercial control [40]. A small concentration of polypropylene carbonate (0.5–1.5 wt%) was added to the wood adhesives to improve the curing behaviour. However, addition of polypropylene carbonate did not significantly improve the mechanical properties of strandboards [41].

6. Phenolic resins from pressure liquefaction liquids

Liquefaction of lingo-celullosic materials represents another route for obtaining phenolic resin precursors. It is generally performed under high pressure at temperatures of $<350\,^{\circ}C$ and followed by a separation process. Russell et al. [42] liquefied a variety of lingo-cellulosic materials including sawdust, woodchips, agricultural residues and peat moss at 290–350 °C and 10–20 MPa in the presence of water and a Na_2CO_3 or $CaCO_3$ catalyst. A phenolic fraction was extracted as follows (see the diagram in Fig. 2): the liquefaction oil is first contacted with diethyl ether resulting in a first soluble and first insoluble fraction. The first soluble fraction is then contacted with aqueous $NaHCO_3$ resulting in a second soluble and a second insoluble fraction. The second insoluble fraction was then contacted with NaOH resulting in a third soluble and a third insoluble fraction. The third soluble fraction was then contacted with HCl resulting in a fourth soluble and a fourth insoluble fraction. The fourth insoluble fraction was then contacted with diethyl ether resulting in a fifth soluble and a fifth insoluble fraction. The fifth soluble fraction was then contacted with water resulting in a phenolics fraction and a sixth soluble fraction. Such multiple steps separations involving complex routes are less attractive economically for industrial applications. Synthesis of phenolic resins was performed by directly reacting the phenolics fraction (100 parts) with 37% formaldehyde solution (1330 parts), water (660 parts) and NaOH catalyst. The phenolic resin was tested on birch veneer plywood. A better bond strength was achieved than for the commercial control, while other measures of quality were not assessed.

Liquefaction of wood followed by a less complex separation process to extract reactive compounds was investigated by Alma et al. [43]. Monarch birch wood waste was first liquefied in a closed autoclave reactor along with phenol, water and NaOH at 250 °C for 1 h. Then the temperature was decreased to 100 °C, and finally to ambient temperature. The initially high temperature of 250 °C was required to minimise the residue left after dissolution, of lignocellulosic feedstocks in phenol using alkali as the catalyst. A reaction time of around 1 h was sufficient to achieve residue minimisation and to keep other parameters, such as non-reacted phenol, combined phenol and the pH of the liquefied mixtures, constant. Aqueous alkali is more effective than water for the liquefaction of biomass in phenol. The dissolution of biomass is at its maximum for a phenol to biomass ratio of 4–6. The ultimate pH of liquefaction is always acidic whether the starting pH is alkaline or acidic. Wood, particularly waste hard wood (birch), is more susceptible to liquefaction than other biomass feedstocks. The dissolution of wood varies significantly with reaction conditions, e.g. pH and temperature, and the nature of metal ions [44].

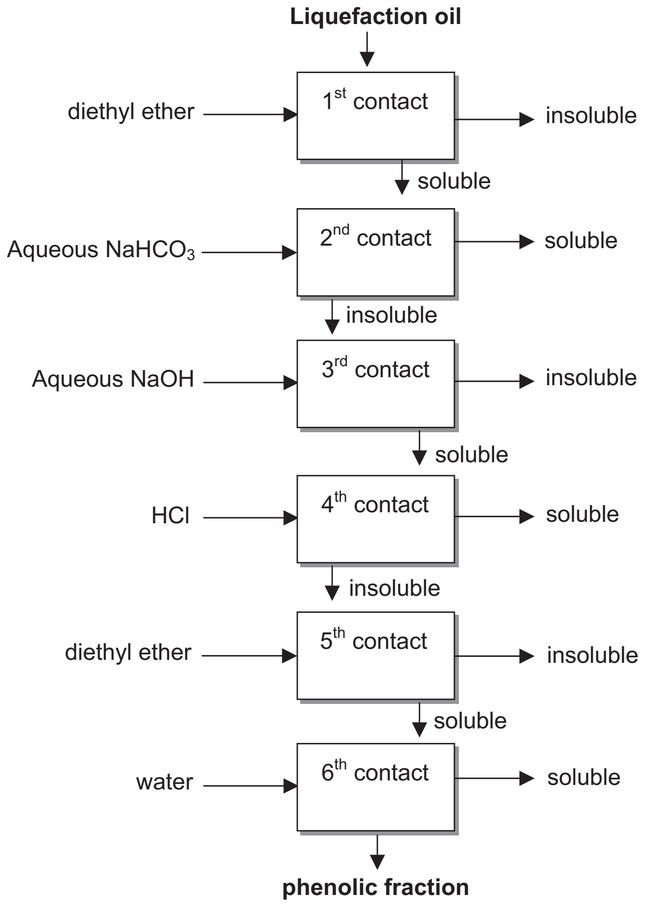


Fig. 2. Schematic diagram of fractionation steps for isolation of phenolic compounds [42].

Sodium hydroxide, a basic catalyst, was used to increase the selectivity of reactive compounds and the phenol promoted degradation of hemicellulose and cellulose through trans-glycosylation forming (hydroxymethyl) furfural compounds in high yields. Liquefaction yielded wood oil containing both reactive compounds and wood residues (3–18.7%). Isolation of the reactive compounds from the liquid mixture was performed by adding methanol, which was then removed from the soluble fraction containing the phenolics by vacuum evaporation. The phenolics fraction was then reacted with formaldehyde to make resole-type resin for a plywood application. The resole resins prepared met Japanese Industrial Standards in terms of dry shear adhesive strengths. To achieve resistance against boiling water the resins need to be upgraded further by using formaldehyde to phenol ratios above 2 and by adding a cross-linking agent such as diphenylmethane diisocyanate.

Birch wood-based liquefied oil was also tested for a Novolac type resin [45]. The birch wood was first phenolated in sulphuric acid used as a catalyst at optimised reaction conditions. Optimum conditions were found at temperatures of 60–150 °C, times of 60–120 min, catalyst concentrations of 1–3% and phenol to wood ratios of 2–5. Methanol

was added to the liquefied mixture, the soluble fraction was neutralised with magnesium oxide and then excess solvent and un-reacted phenol were removed. The concentrated liquid was the Novolac resin. The flow properties of the resin mouldings can be brought to the same level as commercial Novolac resins when a relatively high amount of free phenols is present in the liquefied wood-based resin. This does imply considerably less than 100% phenol substitution. No attempt is presented at estimating actual phenol substitution.

In addition to birch wood waste, preservative treated wood has been explored as a feedstock for phenolics production through liquefaction. Preservative treated wood waste containing creosote (chromated copper arsenate) has been evaluated and liquefied by Shiraishi et al. [46] for phenol-based resin adhesives of both the Novolac and resole varieties. The liquefaction process was performed in phenol with sulphuric acid catalyst at 150 °C for 1 h. After the desired reaction time, the liquefied product was cooled to room temperature, and then diluted by methanol, followed by filtration. Residue obtained from the liquefied creosote-treated wood was 5.8%, which was significantly lower compared to that from the liquefied non-treated birch wood, 17.3%. Based on their results Shiraishi et al. argued that the residual creosote content of the treated wood acted as a reagent co-working with phenol to enhance the liquefaction. Synthesis of resole resins was performed as follows; the creosote treated wood was first liquefied at 150 °C for 1 h. Then the temperature was decreased to 70–90 °C, and formalin (37% aqueous solution) and 33.3% NaOH solution were added to achieve a pH of 10. Molar ratios of formaldehyde to un-reacted phenol ranged from 1.0 to 1.5. The actual resin synthesis was performed at 70–90 °C for 10–120 min under reflux. The polymerisation reaction was terminated by rapid cooling to ambient temperature. The preparation of the Novolac resin was similar to that of the resole, but with no NaOH addition. The liquefied products were dissolved in methanol and neutralised with magnesium oxide. The mixture was concentrated by successive reduced-pressure evaporations at 50 and 180 °C to remove diluting solvent and un-reacted phenol. The Novolac resin was then obtained as a concentrated liquid and stored in a desiccator. The flexural strength and flexural modulus of mouldings made from Novolac resins prepared from liquefied creosote-treated wood were comparable to the results obtained for Novolac resins made from birch wood. The bond quality of pine plywood made from liquefied creosote-treated wood resin was only slightly lower than plywood made from a conventional phenolic resin used as a control. Visual examination of wood failures on broken shear specimens seemed to indicate over-penetration of the resole resin made from liquefied creosote-treated wood. Shiraishi et al. argued that this was probably one of the major causes of lower bond quality. With additional studies of resole formation and glue mix formulations, it was anticipated that a resin adhesive from liquefied creosote-treated wood with improved bond quality could be developed.

Lee [47] investigated wood liquefaction in sub-critical and supercritical phenol. Under the conditions employed, wood liquefaction was very fast. About 90% of the wood was liquefied within 0.5 min, and the combined phenol content of the liquefied wood, including the phenol added to the biomass that is, reached about 75%. With increasing reaction temperature and phenol to wood weight ratio, the amount of methanol-insoluble residue decreased and the total phenol content increased. Molecular weights of the liquid products were from 400 to 600 g/mol with polydispersity of 1.5–2.5. The liquid was composed of low molecular weight components early on in the liquefaction process, but with longer reaction times the molecular weight increased. Properties of the liquefied wood were similar to that obtained from the conventional liquefaction method; moreover the total phenol content

remained the same. Mouldings made using a Novolac resin formulated using this liquefied wood had a comparable flexural strength as the resin obtained via the conventional method.

Waste paper i.e. newsprint containing around 20% lignin was investigated by Ono et al. [48] as a source of phenolics for resole resins. Newsprint was treated in phenol at 150 °C resulting in the functionality of phenolated newsprint to be 1.66 mol/100 g. The phenolated newsprint was then reacted with formaldehyde to make a resole-type resin. The adhesive properties of the resin, such as cure behaviour, resin viscosity and tensile bond strength of the plywood, were comparable to those of a standard phenolic resin.

Liquefaction of waste paper was also studied by Lee and Ohkita [49]. The waste paper included newspaper, box paper and business paper. Newspaper which had the most lignin was more easily liquefied than box paper or business paper which consisted mainly of cellulose with a crystalline structure. Liquefaction was carried out in phenol at 130–170 °C for 20–180 min. Acid catalyst concentration and phenol/waste paper ratio were important parameters in the regulation of the liquefaction. Apparent molecular weight of the liquefied waste paper was strongly dependent on the reaction time, the alteration in the molecular weights was more pronounced for phenolated newspaper with high lignin content, than for phenolated business paper. All phenolated products showed thermal flow properties and reactivity as good as those of phenolated wood and commercial Novolac resins. Thermosetting mouldings obtained from phenolated products and their flexural properties as well as thermal stability were comparable to those of phenolated wood and commercial Novolac resin.

Liquefaction of corn bran was evaluated for the production of a resole-type resin [50]. It was conducted in a stainless-steel autoclave at >1 MPa and 200 °C for 10–60 min. When the reaction was complete, the autoclave was cooled and the reaction mixture was poured into methanol. The methanol-soluble fraction was analysed and also used as a phenolic resin precursor. For the resole resin synthesis, the liquefied oil derived from corn bran was mixed with 37% aqueous formaldehyde and sodium hydroxide, then refluxed at 55–85 °C for 1–4 h. Mild condensation conditions were preferred to prevent the formation of high molecular weight compounds and the consequent deterioration of resin viscosity. The properties of this resole resin namely gel time and viscosity were comparable to those of a conventional resole resin.

7. Phenolic resins from phenolysis of lignins

Lignin from the pulp and paper industry is a low-cost waste product available in large amounts. Consequently, there has been considerable interest in converting it to phenolic precursors for phenol-based resins. Lignin can also be used directly, both as a filler and as a phenol substitute in PF resins. Because of its extremely low reactivity, however, direct use as a phenol substitute requires very long press times and temperatures and is therefore generally not commercially attractive [17]. To produce more reactive phenolic precursors lignin can be processed prior to resin synthesis [15,16]. This paper briefly reviews the use of modified lignins as phenolic precursors for phenol-based resins. Modification of lignins prior to resin synthesis has typically been performed by reacting lignins with phenol in the presence of organic solvents such as methanol or ethanol. This process is called phenolysis.

Organosolv Alcell lignin was used as a replacement for phenol in PF resins [51]. Initially, lignin was allowed to react with phenol before performing a condensation reaction with

formaldehyde. Lignin was added to a mixture of phenol dissolved in ethanol, such that the lignin/phenol weight ratio was varied and known. Phenolysis of the lignin was allowed to proceed at 70 °C for a few hours. Subsequently ethanol was removed from the mixture by vacuum evaporation. A homogenous mixture of lignin and phenol was achieved and its viscosity varied depending on the phenol to lignin ratios. The lignin phenol formaldehyde (LPF) resins exhibited adequate properties such as a curing time and viscosity comparable to those of standard commercial PF resins. These resins were tested on particle boards. Particle boards were made using these resins with up to 30% phenol substituted with the phenolated lignin and demonstrated similar physical and mechanical properties as for standard PF resins. Physical properties measured included internal bonding (IB), modulus of rupture (MOR) and elasticity (MOE) as well as thickness swelling and water absorption. The results indicated that phenol substitution levels of up to 30% in the formulation of the PF resins gave acceptable wood adhesives for constructing particle boards [52]. The fact that phenol is utilised in phenolysis implies that 100% phenol substitution cannot be achieved via this route.

Lignin originated from sugarcane bagasse has been evaluated with regard to the possibility of developing renewable wood adhesives [53]. It was suggested that bagasse lignin has a high number of hydroxyl groups per phenyl-propane unit and hence might have particularly promising potential as a source of phenolic precursors. Bagasse lignin was first extracted through a delignification process which was as follows; ground bagasse and NaOH catalyst were refluxed at 100 °C for 7 h, and the black liquor obtained was filtered to remove suspended pulp fibres, and then the clean liquor was neutralised and the bagasse lignins simultaneously precipitated. Precipitated lignin was then filtered and washed, the wet lignin yield was about 60% based on the initial bagasse weight. This bagasse lignin was then phenolysed at 40 °C for 1 h, a step that was followed by the actual resin synthesis i.e. adding the remaining amounts of phenol, methanol, alkaline catalyst and formaldehyde at 80 °C for 4 h. LPF resins were characterised and tested on specimens prepared from a teak wood–teak wood interface. The wood adhesive was applied on both sides of the interface. The glued samples were then pressed and subsequently conditioned. The results indicated better bonding strength than for the standard PF resin at a phenol substitution level of 50%. Characterisation of the LPF resins demonstrated their structural similarity to the standard resin. It also showed relatively lower thermal stability and temperature required for curing the resins.

Lignosulphonates are derived from the precipitation of black pulping liquor. Their production amounts to about 6% of all lignins from the pulp and paper industry. A third is already used for non-energetic applications and lignosulphonates represent 90% of non-energetic lignin use. Lignosulphonates have also been utilised directly with the Pederson technology. Very high press times of 60–90 s/mm together with press temperatures of 170–235 °C were required and even then further curing at 10 bar for several hours in autoclaves kept at 170–210 °C was necessary [17]. A major issue preventing utilisation in other premium value added applications is the variability of lignin characteristics due to factors such as pulping and recovery conditions and type of feedstock employed. Structural modification of lignosulphonate has been studied for use in a Novolac phenolic resin. Lignosulphonate was phenolated in order to achieve high reactivity of the phenolics towards formaldehyde i.e. phenolics with available *ortho* and *para* units [54]. Lignosulphonate was activated by phenolysis in the presence of oxalic acid catalyst. The mixture was then precipitated by adding acetic acid and washed with ethyl-ether. Optimum

phenolysis conditions were found at 120 °C with a residence time of 3 h and 30% lignosulphonate content. Phenolysis caused fragmentation reactions in the lignosulphonate as shown by a decrease in both molecular weight and polydispersity. These were more pronounced when phenolysis was performed at high temperature and with a long reaction time.

Sulphur-free lignin extracted from steam exploded woods has been deemed to be attractive as more available reactive functional groups are present. The absence of blocked reactive functional groups may be an advantage for various chemical modifications. Sulphur-free lignin extracted from steam exploded white birch pulp was reacted with formaldehyde after phenolysis to produce a renewable phenolic resin [55]. This steam explosion lignin based resin had intrinsic retardation in curing behaviour as compared to a commercial phenolic resin which might be due to its low pH value. Once cured it had excellent bond strength, comparable to standard phenolic resins.

8. Phenolic resins from fractionated pyrolysis liquids

8.1. Fractional condensation

During the slow heating required for conventional distillation, many bio-oil components, including in particular the reactive phenolics of interest for resin manufacture, will polymerise. Consequently, fractional condensation, sometimes under reduced pressure, has been investigated extensively as an alternative means of fractionating the oil.

Pyrolysis of pine sawdust combined with condensation of vapours at different temperatures followed by a coalescing filter has been used to obtain bio oils with high selectivity of reactive compounds [23–26]. Pyrolysis experiments were performed on a unit with a capacity of 10–20 kg/h and at 480–520 °C to produce over 55 wt% of pyrolysis oil on a dry basis. The first condensation stage was a cyclonic condenser chilled with water at 20 °C, the second condensation stage consisted of a vertical vortex tube cooled to 2 °C. The third stage was a glass carboy immersed in a mixed dry-ice and propanol bath, which cooled the product gases to roughly −17 °C. The gas and aerosol stream was then passed to a coalescing filter to remove the aerosols. A bio-oil fraction rich in reactive phenolics was obtained from the second condenser and further treated with organic solvent and basic solutions. Between 20–25 wt% of the dry feed was recovered as phenolics and neutrals after this step. This fraction was used in Novolac and resole resin formulations. At a phenol substitution level of 50% the Novolac resin preparation had a shorter gel time than commercial plywood resins. Another important finding was the ability to reduce the amount of formaldehyde in the resin formulation, around two-thirds of the normal amount was necessary to produce a bio-oil wood adhesive with 50% phenol substitution.

Several condensers for oil collection have also been employed by Kelley et al. [56] from NREL. They pyrolysed softwood in a vortex reactor at 625 °C. The hot vapours exited the reactor system at 455 °C. The initial condensation occurred in a Venturi scrubber which had an inlet temperature of 360–375 °C and typically quenched to 85–90 °C. Following the Venturi scrubber this stream passed through two conventional shell and tube exchangers with temperatures from −5 to 5 °C. Pyrolysis oil was further upgraded by adding water and raising the pH of the oil to 7. After neutralisation the oil fraction was treated with

ethyl acetate. Yields of phenolic/neutral compounds from the raw oil were typically around 35%. At 25% phenol substitution the performance properties of properly formulated phenolic resins were claimed to favourably compare with those of commercial resins.

Fractional condensation to produce a pyrolysis oil fraction rich in reactive phenolics for direct use in resole resins has also been evaluated [37]. A vacuum condensation train was optimised to give good recovery of reactive phenolics. Bark was pyrolysed under vacuum and the vapour condensed in stages. The first condenser gave a phenolics-rich pyrolysis oil having a dew point of about 65–75 °C under 15–20 kPa [37,57]. The researchers suggested that these temperature and pressure ranges were particularly advantageous. Low temperatures were necessary, it was argued, to prevent polymerisation reactions and the formation of highly viscous liquids and low pressures then had to be employed to avoid the condensation of water vapour and of low molecular weight acids and undesirable odorous compounds. This phenolics-rich pyrolysis oil fraction contained around 70 wt% of phenolic compounds such as monophenols, polyphenols, flavanoids, low molecular weight lignins and tannins, around 19 wt% of neutral compounds such as ketones, aldehydes, steroids and furfural derivatives, and around 11 wt% of sugars such as levoglucosan and also some high molecular weight carboxylic acids such as fatty acids. Non-condensed vapours obtained in the above step were further condensed at about 15–30 °C under 15–20 kPa, or at equivalent temperature/pressure thermodynamic conditions, to obtain a further condensate comprising an organic phase in admixture with an aqueous phase. Since the organic phase still contained desirable phenolic compounds that were not condensed in the first condensation step, it was separated from the aqueous phase and then subjected to an evaporation so as to recover a residue comprising a phenolic fraction boiling above 125 °C under atmospheric pressure. Resole resins with a phenol substitution of 40% were prepared with these two phenolic-rich fractions.

Giroux and Freel [30,31] investigated the production and use of renewable resins derived from bark and other biomass residues using rapid destructive distillation that is fast pyrolysis. Product recovery was with two condensers. The first condenser was a direct quenching system and typically gave a liquid recovery equivalent to 50% of the dry feed. A second condenser typically yielded another 20% of the dry feed in liquids. Evaporation at 120 °C was applied to drive off water, acids including acetic acid and odorous and non-resin components (see the schematic diagram in Fig. 3). The patent also claims that the distillation step could provide controlled polymerisation of the oil feedstock while maintaining reactive lignin sites in the resin product. Treatment of the pyrolysis oils by adding water or slight aqueous basic solutions is also included to neutralise the fraction or increase the acidic pH.

8.2. Fractionation of condensed liquids

Mohan et al. [7] have reviewed fractionation processes aimed at the isolation of chemicals such as syringol or the separation of a phenolics-rich fraction, acids and neutrals from pyrolysis oils derived from a variety of biomass feedstocks and reaction conditions. The present review is only concerned with fractionations specifically performed for the production of phenol-based resins, but within that more narrow scope a greater number of references is dealt with than by Mohan et al.

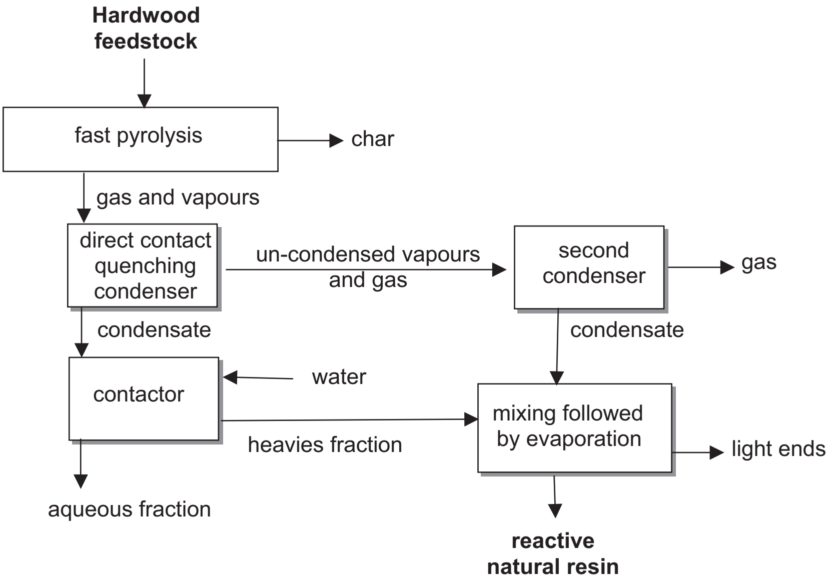


Fig. 3. Schematic diagram of typical isolation steps of reactive natural resins [30,31].

8.2.1. Liquid–liquid extractions

Gallivan and Matschei [58] from American Can. Co. investigated a method of fractionating pyrolysis oils to obtain a phenolic fraction which was suitable as a total or partial substitute for phenol in making PF resins. Pyrolysis oils were obtained from the pyrolysis of wastes such as bark, sawdust, tree-tops and limbs. The fractionation method (see the schematic diagram in Fig. 4) comprises mixing the oil with NaOH to a pH level at which the neutral fraction of the oil is selectively soluble in a solvent such as methylene chloride or ether. The mixture is extracted with the solvent to obtain a first extract containing the solvent and the neutral fraction, and a first raffinate containing the remaining fractions of the oil, i.e. phenolics, organic acid fractions and amorphous residues. The neutral fraction is recovered by distillation and the first raffinate is mixed with sulphuric acid to lower its pH to a level at which the phenolic fraction is selectively soluble in the solvent. This raffinate is extracted with the solvent to obtain a second extract containing the solvent and the phenolic fraction and a second raffinate containing the organic acids and the residues. The phenolic fraction is recovered by distillation and the second raffinate is mixed with sulphuric acid to lower its pH to a level at which the organic acids are selectively soluble in the solvent. After separating the residues, the second raffinate is extracted with the solvent to obtain a third extract, which is distilled to recover the organic acid fraction of the oil. The complexity of solvent extraction routes limits the industrial application of such a process. From the method applied roughly 33% phenolic, 32% neutral and 24% acid fractions could be recovered. The phenolic fraction may be used for partial or total replacement of pure phenol in making PF resins. A resin was formulated by Gallivan and Matschei using the whole phenolic fraction (25 g), 37% formaldehyde (87 g), water and

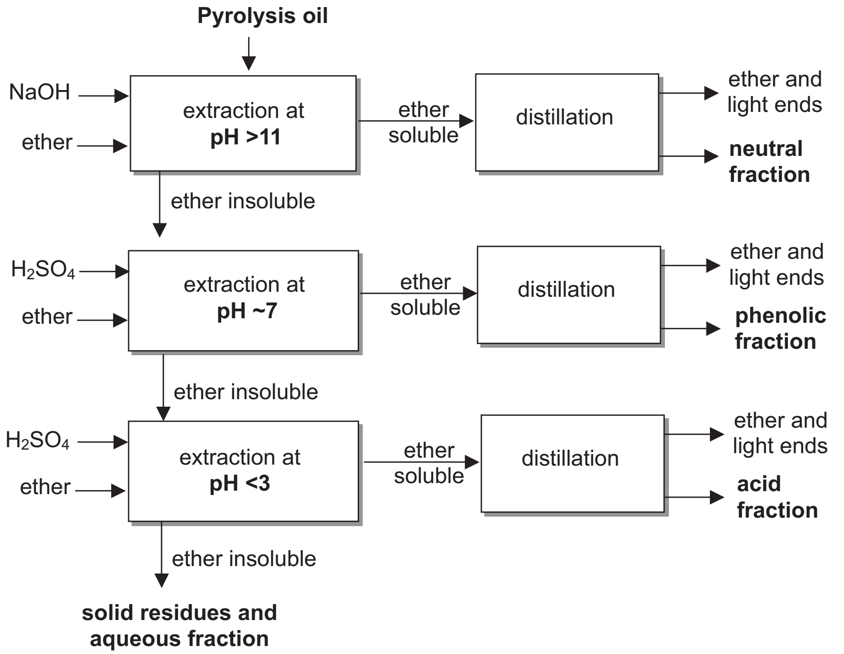


Fig. 4. Schematic diagram of fractionation steps for isolation of phenolic compounds [58].

NaOH catalyst. The mixture was refluxed for less than 1 h. The resulting adhesive was used to laminate veneer panels (plywood), which were tested for wood failure. The phenolic-fraction-based adhesive showed comparable results with those made from petroleum PF resin.

Separation of reactive phenols and neutral fractions through liquid–liquid fractionation in several steps has also been investigated by Chum et al. [23–26] for the preparation of PF resole resins. The bio-oil was obtained by fast pyrolysis of lignocellulosic materials in a vortex reactor tube at 450–600 °C with vapour residence times of a few seconds. The fractionating process (see the diagram in Fig. 5) involves a series of liquid–liquid extraction steps. Initially the phenolic compounds are partitioned from the pyrolysis oil into an organic phase using ethyl acetate and the organic phase is then treated with an aqueous alkali metal bicarbonate solution to remove acids yielding a fraction containing phenolics and neutrals. After evaporation this fraction may be used in resole-type resins. The yield of the phenolic and neutrals fraction from the extraction procedure is about 30% of the fast-pyrolysis oil derived from sawdust and about 50% of the oil derived from bark. Phenolic compounds/neutral (P/N) fractions have molecular weights of 100–800 g/mol. The fraction also contains many compounds with aldehyde groups. This is advantageous, as less formaldehyde is needed for resin formulations. Preliminary results revealed that the fractionated pyrolysis oils could be used within P/F resin compositions, as P/N containing resins exhibited equivalent gel times as noted for standard P/F resins. Novolac resins and moulding compositions were also prepared with P/N fractions to substitute phenol and formaldehyde.

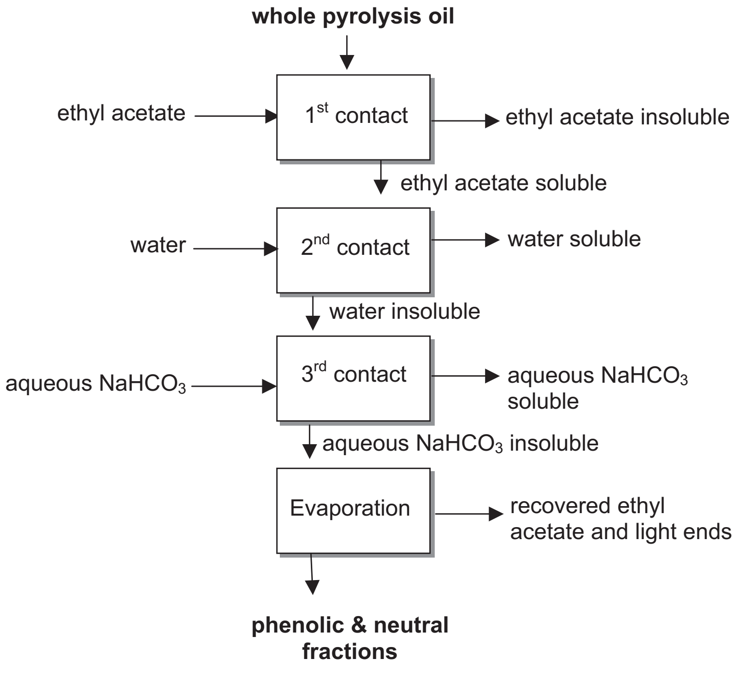


Fig. 5. Schematic diagram of fractionation steps for isolation of phenolic and neutral compounds [23–26].

8.2.2. *Precipitation of pyrolytic lignins*

Pyrolytic lignins, which are considered to be the water insoluble part of pyrolysis oils, can be obtained by precipitation in water, as explained earlier. After separation and drying, a fine homogeneous powder is obtained. Pyrolytic lignins are close to exclusively composed phenolic compounds. Pyrolytic lignins of pyrolysis oils precipitated from different fast pyrolysis processes have been characterised [10,11] and found to be similar to the corresponding milled wood lignins. Pyrolytic lignins derived from beech pyrolysis oil yield guaiacol, 4-methylguaiacol, syringol, 4-methylsyringol, vanillin, 4-vinylsyringol, *t*-4-propenylsyringol, syringaldehyde, acetosyringone, *t*-coniferylalcohol and *t*-sinapylalcohol. Pyrolytic lignin derived from pine softwood, on the other hand, mainly yields high concentrations of 4-methylguaiacol and *t*-isoeugenol. Most of these pyrolytic lignins are likely oligomeric alkylated aromatic units probably largely linked by C–C bonds. Scott [59] prepared pyrolytic lignins from pyrolysis oils using precipitation and centrifugation or filtration of the non-aqueous fraction. Adhesive formulations prepared using the lignins were found to be inferior to the standard P/F resin in both colour and odour, and required long press times in order to avoid de-lamination of wafer-boards. Tests indicated that none of the pyrolytic lignin samples met the internal bond (IB) test requirement. Low reactivity with formaldehyde may be related to the number of available active sites for reacting formaldehyde with phenol which are at the 2, 4 and 6 positions, i.e. the *ortho* and *para* positions [10,28,54,59]. For example, as has already been suggested earlier, pyrolytic lignins with syringols have only the *para* site remaining for reaction with aldehydes, which will result in chain-termination of the resultant phenol/aldehyde oligomers [60] (see also Fig. 1).

9. Summary tables

Production and fractionation methods for fast and vacuum pyrolysis are summarised in Table 3. Key process conditions as well as phenolic and liquid yields are given.

A selection of renewable phenolic resins covered in this review are listed in Table 4. The table shows feedstocks used, processes employed, fractions applied in the resin and degrees of phenol substitution investigated. The properties of phenol-based resins prepared using renewable phenolics (and formaldehyde substitutes in some cases) are compared to those of the commercial resins. Moreover information about tests performed on panels produced using these renewable resins is presented.

Table 3
Production of phenolic compounds from pyrolysis of biomass and their isolation methods

Feedstock	Thermochemical conversion process	Method of phenolic compounds isolation	Phenolics (% per fraction)	Pyrolysis oil (wt% of dry feedstock)	Refs.
Softwood bark	Vacuum pyrolysis at 505 °C, 18 kPa	Fractional condensation	No organic acids	28	[5,39–41]
Pine, bark, softwood, hardwood, grasses	Flash pyrolysis in a vortex reactor at 450–600 °C	Liquid–liquid separation	30	55	[23–26]
Bark, sawdust, treetops, limbs and the like	Pyrolysis	Liquid–liquid separation/ distillation	33	na	[58]
Wood, bark, forest residues, wood industry residues or other biomass	Fast pyrolysis, RTP process	Distillation/ evaporation	<64	40–60	[31–33]
Mixed hardwoods	Pyrolysis in an air-blown bubbling fluidised bed at 590 °C	No product separation	Around 82 mol% of the oil	Low	[28,29]
Ground softwood	Fast pyrolysis in a vortex reactor at 625 °C followed by condensation train at diff. T's	Liquid extraction	35	na	[56]
Softwood bark	Vacuum pyrolysis at <550 °C, <50 kPa, pyrocycling process	Fractional condensation at 65 to 75 °C, 15–20 kPa then at 15 °C and partly liquid–liquid separation	70	<30	[37]
Woods	Pyrolysis	Precipitation of pyrolytic lignin	100	na	[59]

Table 4
Renewable resins prepared using phenolics from the thermochemical conversion of biomass and processed lignins

Production of phenolics			Resin formulations					Refs.
Feed materials	Process	Phenolic precursors	PF resin type	Phenol substitution attempted	Compared to standard P/F resin	Wood panel type	Panel performance compared to the standard	
Wood waste (Monarch birch)	Liquefaction at 150 °C	Phenolated wood, the soluble fraction in MeOH	Resole and novolac	100%	Meet Japanese Industrial standards	Plywood	Comparable dry shear adhesive strength	[43,45]
Bark residues	Vacuum pyrolysis at 505 °C 18 kPa	Whole oil, no organic acids	Resole	25%, 50%	Meet Canadian standards, with an accelerator e.g. poly-propylene carbonate	Strandboards	Better mechanical strength (i.e. IB, MOR, MOE)	[5,39–41]
Organosolv lignin	Liquefaction	Phenolated lignin	Resole	30%	Similar curing behaviour	Particle-boards	Similar physical and mechanical properties	[51,52]
Pine, bark, softwood, hardwood	Pyrolysis in a vortex ablative reactor	Bio-oil fraction	Resole and novolac	Up to 75%	Equivalent gel times	Plywood	na	[23-26]
Bark, sawdust, treetops, limbs and the like	Pyrolysis (no further details)	Phenolic fraction	Resole	100%	Equivalent viscosity of finished resins	Plywood	Comparable result on wood failure test	[58]
Wood, bark, forest and wood industrial residues or other biomass	Flash pyrolysis, Ensyn RTP process	Whole bio-oil or fraction, <64% phenolics	Resole and urea-based resins	60%	Equivalent	Laminated wood, plywood, particleboard, high density particleboard MDF, OSB, hardboard and wafer board	Equivalent	[30,31]
Waste paper	Liquefaction at 130–170 °C	Phenolated paper waste	Novolac	100%	Equivalent	na	na	[49]

Table 4 (*continued*)

Production of phenolics			Resin formulations					Refs.
Feed materials	Process	Phenolic precursors	PF resin type	Phenol substitution attempted	Compared to standard P/F resin	Wood panel type	Panel performance compared to the standard	
Corn bran	Liquefaction at >1 MPa, 200 °C	Phenolated corn bran, the soluble fraction in MeOH	Resole	100%	Comparable gel time, viscosity	na	na	[50]
Ground softwood	Fast pyrolysis at 625 °C in an ablative reactor with condensation trains at diff. T's	Bio oil fraction, 35% phenolics	Resole	25%		Wood composites	Comparable mechanical properties	[56]
Bagasse	Liquefaction at 80 °C	Phenolated lignin	Resole	50%	Lower thermal stability	na	na	[53]
Wood	Liquefaction in supercritical phenol	Liquefied wood	Novolac	100%	Comparable	na	na	[47]
Softwood bark	Na	Whole pyrolysis oil	Resole	50%	Comparable	OSB, plywood	Better performance	[34]
Lignin from steam explosion of birch	Liquefaction at 170 °C	Phenolated lignin	Resole	30%	Slow curing rate	na	na	[55]
Lignin from newsprint	Liquefaction in phenol at 150 °C	Phenolated paper waste, 20% lignin	Resole	About 10%	Comparable	Plywood	Comparable	[48]
Softwood bark wastes	Vac. pyrolysis at <550 °C, 50 kPa, Pyruvac Pyrocycling process	Whole bio-oil, 70% phenolics	Resole	40%	na	OSB	Better mechanical strength (i.e. IB, torsion shear)	[37–41]
Creosote treated wood waste	Liquefaction at 150 °C	Phenolated wood waste	Novolac	100%	na	Pine plywood	Comparable	[46]
Wood	Precipitation of pyrolytic lignin from bio-oils	Pyrolytic lignin	Resole	100%	Odour and colour disadvantages	Wafer-board	Long press times and high de-	[59]

10. Conclusions

Interest in renewable resins is motivated by the large availability of lignin-containing biomass feedstocks, particularly low-cost waste streams, the relatively high price commanded by phenol and more recently environmental considerations.

There are, however, significant hurdles that have so far prevented widespread commercialisation. The failure of the Pederson technology mentioned earlier is illustrative. In spite of good board properties, commercial use eventually ceased due to the high-processing costs inherent in the long press times and high temperatures that were required [17].

Phenolics from the thermochemical processing of biomass are generally less reactive than pure phenol, as they tend to have an average of two or fewer positions available for polymerisation, while three positions are available in phenol. Furthermore, liquids obtained through thermochemical degradation of biomass also contain sugars, acids and other undesirable chemicals. These act like fillers and may have a negative impact on such board properties as resistance against swelling.

As this survey shows, considerable effort has gone into varying process and recovery conditions to obtain a phenolics-rich product with high reactivity that is equivalent in all respects to standard phenol-based resins, while simultaneously being of lower cost and more environmentally acceptable.

While substantial progress has been made, this twin challenge has so far eluded the research community. Use of a whole product, be it a bio-oil, liquefaction oil or lignosulphonates, is preferable from a cost point of view. Generally, only substitutions of around 50% or less are then feasible without significantly degrading important resin properties. In most cases, the panels will then perform relatively well, sometimes even better than for commercial resins, on measures of bond strength, while performance as measured by required press times or dimensional stability is usually much more problematic.

Fractionation to reject acids, sugars and odorous compounds in particular and to concentrate reactive phenolics allow higher substitutions, but even then low reactivity makes it hard to maintain commercially used press times. Fractionation, especially by complex solvent extraction, also tends to be quite costly, and gives lower yield, making the issue of co-product utilisation or disposal more significant.

Due to recent progress, and environmental and cost pressures, however, key players in PF resins and board manufacture continue to be interested in the commercialisation of phenolics from thermochemical conversion of biomass [4]. Particular interest is focused on waste lignins from the pulp and paper industry, and also on bark, both because it is a readily available waste from the debarking of wood performed by many panel manufacturers, and also because it is relatively high in lignin and phenolic extractives.

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